

COMBUSTION OF THE BUTANOL ISOMERS: REACTION PATHWAYS AT ELEVATED PRESSURES FROM LOW-TO-HIGH TEMPERATURES

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Abstract

A reaction mechanism for the combustion of the four butanol isomers is presented. The mechanism's predicted ignition delay as a function of temperature and pressure is validated against previously-reported measurements performed in a rapid compression machine and high-pressure shock tubes. The dominant pathways of the different isomers, under the differing experimental conditions, are discussed. Particular emphasis is placed on the mechanism's pressure-dependent kinetics and the hydrogen abstraction reactions of butanol by hydroperoxy radical. To the authors' knowledge, this mechanism is the first to predict the ignition delay of 1-butanol reasonably well under the rapid compression machine experimental conditions.

Keywords

Butanol isomers, Reaction mechanism, Pressure-dependent kinetics

Introduction

The feasibility of alternative fuels as additives or alternatives to conventional fuel is being assessed; particular emphasis has been placed on compounds derived from bio-mass, oxygenated hydrocarbons. One of the more heavily studied oxygenated hydrocarbons is alcohol compounds: while ethanol has been used as a fuel additive for decades, recent emphasis has been placed on studying the four-carbon alcohol, butanol. BP and DuPont have a joint venture, Butamax (2011), focusing on the

production of the primary butanol isomers, 1- and iso-butanol.

Considerable effort has been expended recently to understand the reactive pathways of the butanol isomers. Moss et al. (2008) proposed oxidation reaction mechanisms for all four isomers, validating the model against their ignition delay measurements. Dagaut et al. (2009) proposed a reaction mechanism for 1-butanol which was validated against their 10-atm jet-stirred reactor

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experiments; Sarathy et al. (2009) extended this mechanism to include new experiments: 1-atm jet-stirred reactor and opposed-flow flame speciation measurements, in addition to laminar burning velocity measurements at atmospheric pressure. Black et al. (2010) proposed a reaction mechanism for 1-butanol, validating their model against their ignition delay measurements, in addition to the Dagaut et al. 10-atm jet-stirred reactor speciation data. Veloo et al. (2010) proposed a reaction mechanism, validated against their laminar burning velocity and extinction strain rate measurements. Grana et al. (2010) proposed a reaction mechanism for all four isomers, validating their model against most of the previously mentioned datasets in addition to their own opposed-flow flame speciation data.

Harper et al. (2011) proposed a reaction mechanism for 1-butanol, validating their model against the Moss et al., Dagaut et al., Sarathy et al., and Black et al. datasets, in addition to their own pyrolysis speciation data and the butanol-doped methane diffusion flames of McEnally and Pfefferle (2005). Van Geem et al. (2010) extended this model to include the secondary and tertiary alcohol, 2- and tert-butanol, respectively.

Although several oxidation mechanisms exist for the butanol isomers, all were validated for high-temperature chemistry; furthermore, none of the validation targets were at pressures exceeding 10 atmospheres. Recent studies by Weber et al. (2011A, 2011B), Heufer et al. (2011), and Stranic et al. (2011) suggest that the mechanisms require further understanding at elevated pressures and low-to-intermediate temperatures.

Weber et al. (2011A) recently measured the ignition delay of 1-butanol at elevated pressures in a rapid compression machine. In their discussion, Weber et al. compared their experimental measurements of ignition delay against several 1-butanol mechanisms' predicted ignition delays. Through this analysis, Weber et al. concluded that the current 1-butanol models were insufficient for the low-temperature, elevated pressure conditions of the rapid compression machine. In particular, most of the kinetic models were sensitive to the abstraction of 1-butanol by HO_2 . Weber et al. (2011B) have also measured the ignition delay of iso- and tert-butanol in their rapid compression machine under similar experimental conditions. Heufer et al. (2011), in their shock tube investigations at low temperatures and elevated pressures, also concluded the current 1-butanol reaction mechanisms were sensitive to the abstraction of 1-butanol by HO_2 . Stranic et al. (2011) have recently measured the ignition delay of all four butanol isomers at reflected shock pressures ranging from 1-42 atm. The higher-pressure experiments are the first of their kind for the butanol isomers, for the range of reflected temperatures studied.

Computation Methodology

The proposed reaction mechanism is an extension of the model published by Van Geem et al. (2010). All pressure-dependent kinetics have been updated using the RMG software (2010), utilizing the steady-state master equation method of Green and Bhatti (2007) for estimating pressure-dependent kinetics. Additionally, the model proposed by Van Geem et al. has been extended to include peroxy chemistry by employing the published mechanism as a Seed Mechanism within the RMG software. RMG simulations were run for low temperatures (680 – 800 K) and elevated pressures (15 – 30 bar), reflecting the experimental conditions of Weber et al. (2011A).

Moreover, the H-abstraction kinetics of HO_2 abstracting all distinct C-H hydrogens from all four butanol isomers (four for 1- and 2-butanol, three for isobutanol, and one for tert-butanol) were calculated using quantum chemistry. The single-point energies, geometries, and frequencies for all reactants, products, and transition states were calculated using the CBS-QB3 calculations. The rate coefficients were calculated using conventional transition state theory. An asymmetric Eckart tunneling correction was assumed and the RRHO approximation was employed in calculating the vibrational partition function; a one-dimensional hindered rotor correction was implemented for the low-frequency ($< \sim 300 \text{ cm}^{-1}$) torsional modes.

The simulations for all shock tube and rapid compression machine experiments were performed in CHEMKIN (2010). The closed homogeneous batch reactor model was employed, assuming adiabatic, isochoric conditions. The ignition delay was defined as the time that maximized the $[\text{C}_2\text{H}] * [\text{O}]$ curve; this definition of ignition delay produced similar results to the time to reach half the maximum $[\text{OH}]$ concentration, and to the time to maximum rate of pressure rise.

Results

Shock Tubes

The mechanism's predicted ignition delay for the Stranic et al.'s $\phi=1.0$ dataset for 1- and tert-butanol is shown in Figure 1. Overall, the predictions for the 1- and tert-butanol isomers are in good agreement with the experimental data, across all temperatures and pressures.

Focusing on the simulations with initial pressure of 42 atm and initial temperature of 1175 K:

1-Butanol is consumed primarily through H-abstraction by OH radical, forming 1-hydroxybutyl or 1-hydroxybut-2-yl radical; the latter radical undergoes β -scission to form 1-butene and OH radical. 1-hydroxybutyl radical reacts with O_2 to form HO_2 and butanal. After losing its aldehydic hydrogen via H-abstraction by OH radical, butanal reacts to form n-propyl radical and CO; n-

propyl leads to methyl production which reacts with HO_2 to form OH and methoxy radical. Methoxy radical readily forms formaldehyde and H atom, through β -scission.

tert-Butanol is consumed primarily via H-abstraction by OH, producing 2-hydroxy-2-methylpropyl radical; the dehydration to iso-butene and H_2O is also a significant decomposition pathway. The 2-hydroxy-2-methylpropyl radical undergoes β -scission, forming propen-2-ol and methyl radical; the β -scission forming iso-butene and OH also contributes to the radical's depletion. Propen-2-ol tautomerizes to acetone, which reacts to methyl and acetyl radical via C-C bond fission.

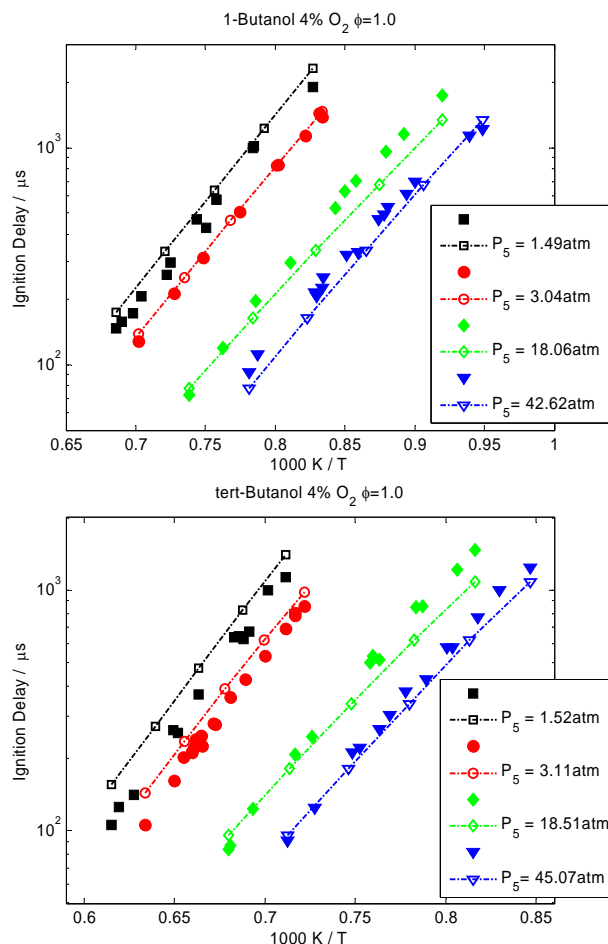


Figure 1. The predicted (lines with open shapes) and experimental (filled shapes, from Stranic et al. 2011) ignition delay of 1- (top) and tert-butanol (bottom).

The mechanism's predicted ignition delay for the Heufer et al. dataset is shown in Figure 2; overall, the mechanism's predictions are in good agreement with the experimental data. Focusing on the simulations at 40 bar, notice that the highest reflected shock temperature of Heufer et al. is similar to the lowest reflected shock temperature of Stranic et al. At the lowest temperature (770 K), the predicted dominant pathway is nearly identical to the pathway discussed previously in the Shock

Tubes section; the only exception is that HO_2 , instead of OH radical, abstracts the aldehydic hydrogen of butanal. At the highest temperature of Heufer et al. (1050 K), the 1-butanol decomposition pathway is similar to the previous case, with the abstraction of butanal by OH and HO_2 predicted to be equally important.

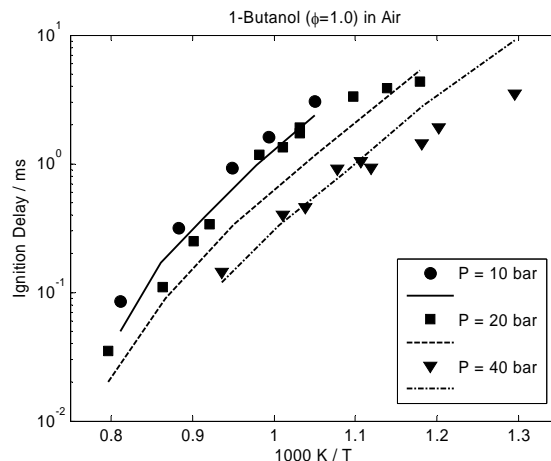


Figure 2. The predicted (lines) and experimental (filled shapes, from Heufer et al. 2011) ignition delay of 1-butanol.

Rapid Compression Machine

The mechanism's predicted ignition delay for some of the Weber et al. experiments is shown in Figure 3. Overall, the mechanism's predictions are in reasonable agreement with the experimental data.

For similar conditions, namely a compressed pressure of 15 bar and an equivalence ratio of one, the combustion properties of tert-butanol are markedly different from 1-butanol: the experimental ignition delay is longer by a factor of two at higher temperatures and nearly an order of magnitude longer at lower temperatures.

At a compressed temperature of 800 K, the dominant decomposition pathway for tert-butanol is predicted to be similar to the pathway discussed in the Shock Tubes section, up to the formation of propen-2-ol. For the rapid compression machine, CH_3OO radical abstracts from the primary site of propen-2-ol, forming 2-oxopropyl radical and CH_3OOH ; this species undergoes O-O bond fission, the predicted chain branching reaction for this system, forming OH and methoxy radicals.

The dominant decomposition pathway for 1-butanol is also predicted to be the same as discussed in the Shock Tubes section. The exception is that HO_2 , instead of OH, abstracts the aldehydic hydrogen of butanal, thus producing H_2O_2 . The O-O bond fission of H_2O_2 , the predicted chain branching reaction for the 1-butanol system, forms two OH radicals.

Although the initial $\text{C}_4\text{H}_9\text{O}$ radical from 1-butanol leads to the formation of HO_2 radical through

disproportionation with O_2 , the initial C_4H_9O radical from tert-butanol cannot follow the same pathway; the carbon adjacent to the radical is not bonded to any hydrogen atoms. This results in the O-O bond fission of CH_3OOH being a significant chain branching reaction for tert-butanol combustion, in contrast to the O-O bond fission of H_2O_2 for 1-butanol combustion.

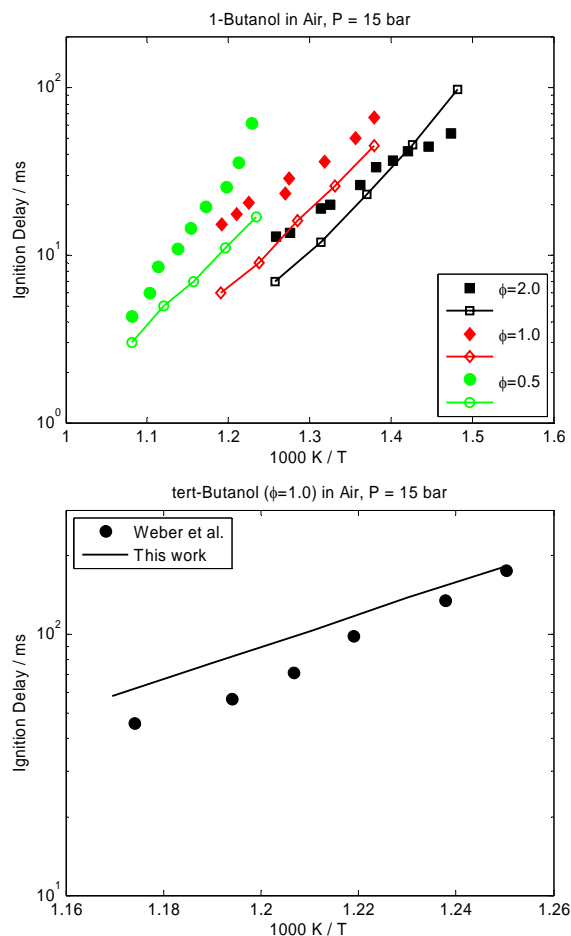


Figure 3. The predicted (lines with open shapes) and experimental (filled shapes, from Weber et al.) ignition delay of 1- (top) and tert-butanol (bottom).

Conclusions

The proposed butanol combustion reaction mechanism has been validated against previously-reported ignition delay measurements from a rapid compression machine and high-pressure shock tubes. The difference in decomposition pathways of 1- and tert-butanol combustion at elevated pressures (15 – 42 bar), over a range of temperatures (700 – 1450 K), has been discussed.

Acknowledgments

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References

- Black, G., Curran, H. J., Pichon, S., Simmie, J. M., Zhukov, V. (2010). Bio-butanol: Combustion properties and detailed chemical kinetic model. *Combust. Flame*, 157, 363.
- Butamax Advanced Biofuels LLC, <http://www.butamax.com/>, accessed January 11, 2011.
- CHEMKIN 10101, Reaction Design: San Diego, 2010.
- Dagaut, P., Sarathy, S. M., Thomson, M. J. (2009). A chemical kinetic study of n-butanol oxidation at elevated pressure in a jet stirred reactor. *Proc. Combust. Inst.*, 32, 229.
- Grana, R., Frassoldati, A., Faravelli, T., Niemann, U., Ranzi, E., Seiser, R., Cattolica, R., Seshadri, K. (2010). An experimental and kinetic modeling study of combustion of isomers of butanol. *Combust. Flame*, 157, 2137.
- Green, N. J. B., Bhatti, Z. A. (2007). Steady-state master equation methods. *Phys. Chem. Chem. Phys.*, 9, 4275.
- Harper, M. R., Van Geem, K. M., Pyl, S. P., Marin, G. B., Green, W. H. (2011). Comprehensive reaction mechanism for n-butanol pyrolysis and combustion. *Combust. Flame*, 158, 16.
- Heufer, K. A., Fernandes, R. X., Olivier, H., Beeckmann, J., Roehls, O., Peters, N. (2011). Shock tube investigations of ignition delays of n-butanol at elevated pressures between 770 and 1250 K. *Proc. Combust. Inst.*, 33, 359.
- McEnally, C. S., Pfefferle, L. D. (2005) Fuel decomposition and hydrocarbon growth processes for oxygenated hydrocarbons: butyl alcohols. *Proc. Combust. Inst.*, 30, 1363.
- Moss, J. T., Berkowitz, A. M., Oehlschlaeger, M. A., Biet, J., Warth, V., Glaude, P. A., Battin-Leclerc, F. (2008). An experimental and kinetic modeling study of the oxidation of the four isomers of butanol. *J. Phys. Chem. A*, 112, 10843.
- RMG - Reaction Mechanism Generator, rmg.sourceforge.net/ 2010.
- Sarathy, S. M., Thomson, M. J., Togbe, C., Dagaut, P., Halter, F., Mounaim-Rousselle, C. (2009). An experimental and kinetic modeling study of n-butanol combustion. *Combust. Flame*, 156, 852.
- Stranic, I., Davidson, D. F., Hanson, R. K. (2011). Shock tube measurements of ignition delay time for the butanol isomers. In preparation.
- Van Geem, K. M., Pyl, S. P., Marin, G. B., Harper, M. R., Green, W. H. (2010). Accurate high-temperature reaction networks for alternative fuels: butanol isomers. *Ind. Eng. Chem. Res.*, 49, 10399.
- Veloo, P. S., Wang, Y. L., Egolfopoulos, F. N., Westbrook, C. K. (2010). A comparative experimental and computational study of methanol, ethanol, and n-butanol flames. *Combust. Flame*, 157, 1989.
- Weber, B. W., Kumar, K., Zhang, Y., Sung, C.-J. (2011A). Autoignition of n-Butanol at elevated pressure and low

to intermediate temperature. *Combust. Flame*, under review

Weber, B. W., Kumar, K., Sung, C.-J. (2011B). Autoignition of butanol isomers at low to intermediate temperature and elevated pressure. 49th AIAA Aerospace Sciences Meeting, Paper No. AIAA-2011-0316